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1 Supporting information of "Study on the effect of NH₃ on

2 the solubility of KCl and NH₄Cl – from roscopic view"

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Phase diagram of KCl-NH₄Cl-H₂O system with different ammonia 1 concentration: 2



Fig.S1. Phase diagrams of the KCl-NH₄Cl-NH₃-H₂O system at 298.15 K under 5 different NH₃ concentrations: (a) 5% NH₃; (b) 15% NH₃; (c) 23% NH₃. A: NH₄Cl, B: 6 KCl, C: H₂O [4] 7

Solution Preparation Process: Measure 15 mL of water into a stoppered light 8 conical flask, weigh, add 1 mL of sample, immediately cover the stopper, weigh again, 9 the two weighings must be accurate to 0.0001 g, add 40 mL of water, add 2 drops of 10 methyl red-methylene blue mixed indicator solution with hydrochloric acid standard 11 titration solution [c(HCl) = 0.5 mol/L] titration to the solution is red. Temperature-12

1 controlled treatment throughout the solution preparation process.

$$w = \frac{VcM}{m \times 1000} \times 100 \tag{1}$$

V is the numerical value of the volume of the standard titration solution of hydrochloric acid in milliliters (mL); *c* is the exact numerical value of the concentration of the standard titration solution of hydrochloric acid in moles per liter (mol/L); *M* is the numerical value of the molar mass of ammonia in grams per mole (g/mol), $M(NH_3) = 17.03$; and m is the numerical value of the sample mass in grams 7 (g).

8 Summary of Force Field Parameters for Atoms in Molecular Dynamics 9 Simulation Models: Table.S1 presents the detailed force field parameters of various 10 atoms used in constructing the simulation model during the molecular dynamics 11 simulations conducted in this study.

12 Table S1. Overview of force field parameters for model atoms in molecular dynamics

13 simulations

Epsilon (kJ/mol)	Sigma (nm)	Charge (e)	Mass (g/mol)
0.4184	0.334	+1	39.098
0.4928	0.440	-1	35.453
0.7112	0.325	-1.020	14.007
0.000	0.240	+0.340	1.008
0.6360	0.316	-0.820	15.999
0.000	0.000	+0.410	1.008
0.7113	0.325	+0.28	14.007
0.192	0.240	+0.18	1.008
	Epsilon (kJ/mol) 0.4184 0.4928 0.7112 0.000 0.6360 0.000 0.7113 0.192	Epsilon (kJ/mol)Sigma (nm)0.41840.3340.49280.4400.71120.3250.0000.2400.63600.3160.0000.0000.71130.3250.1920.240	Epsilon (kJ/mol)Sigma (nm)Charge (e)0.41840.334+10.49280.440-10.71120.325-1.0200.0000.240+0.3400.63600.316-0.8200.0000.000+0.4100.71130.325+0.280.1920.240+0.18

1 X-ray scattering results: X-ray scattering results of single KCl-NH₃-H₂O and



2 $NH_4Cl-NH_3-H_2O$ solutions are shown in **Figs.S2** and **S3**.

3 Fig.S2. X-ray scattering pattern of saturated KCl-NH₃-H₂O solution: (a) overall





5 Fig.S3. X-ray scattering pattern of saturated NH₄Cl-NH₃-H₂O solution: (a) overall
6 picture; (b) partial magnification.

From Figs.S2 and S3, it can be seen that with the increase of ammonia
concentration in the solution, the two signals of the shoulder peak near 18° and the
diffuse peak near 30° of the single KCl-NH₃-H₂O and NH₄Cl-NH₃-H₂O solutions
showed a decreasing trend. The positions of the main peaks located near 13° are all

gradually shifted to the direction of low angle, as shown by the shift of the main peak
 position from 13.56° to 13.16° for the KCl-NH₃-H₂O solution and from 13.21° to
 13.01° for the NH₄Cl-NH₃-H₂O solution.

The X-ray scattering data were processed using PDF theory to obtain F(Q). The
F(Q) obtained for saturated KCl-NH₃-H₂O and NH₄Cl-NH₃-H₂O solutions at the
BL14B1 line station are shown in Figs. S4 and S5, respectively.



8 Fig.S4. Difference structure function of saturated KCl-NH₃-H₂O solution.



1 Fig.S5. Difference structure function of saturated NH₄Cl-NH₃-H₂O solution.

As can be seen from Figs.S4 and S5, with the increase of ammonia concentration, 2 the peak intensity of the KCl-NH₃-H₂O solution located at Q = 2.20 Å⁻¹ gradually 3 enhanced, and a more obvious double peak appeared near Q = 2.74 Å⁻¹; the peak 4 intensity of the NH₄Cl-NH₃-H₂O solution at 2.15 Å⁻¹ gradually enhanced, and a more 5 obvious double peak appeared at the peak located near Q = 2.66 Å⁻¹ as well. Obvious 6 double peak. The addition of both systems reflects the gradual disruption of the 7 hydrogen bonding network due to the increase in solute concentration. With the 8 increase of ammonia concentration, the peak located near Q = 4.65 Å⁻¹ for KCl-NH₃-9 H₂O solution shifted to a higher wavelength (from 4.65 Å⁻¹ to 4.85 Å⁻¹), and the peak 10 located near Q = 4.52 Å⁻¹ for NH₄Cl-NH₃-H₂O solution shifted to a higher 11 wavelength (from 4.52 Å⁻¹ to 4.72 Å⁻¹), which is shown by the above analysis. , the 12 saturated KCl-NH₃-H₂O and NH₄Cl-NH₃-H₂O solutions played an obvious 13 destructive effect on the hydrogen bonding network in water, and this destructive 14

1 effect became more and more intense with the increase of ammonia concentration.



2 Raman spectra results:



4 Fig.S6. Raman spectra of KCl-NH₃-H₂O (5%) mixed solution with different mass









13 Fig.S9. Raman spectra and local magnification of NH₄Cl-NH₃-H₂O (5%) mixed

14 solutions with different mass fractions.



1 Fig.S10. Raman spectra and local magnification of NH₄Cl-NH₃-H₂O (10%) mixed

3320

3440



2800

2 solutions with different mass fractions.

1200

1600

2000

2400

Raman shift/cm⁻¹



4 Fig.S11. Raman spectra and local magnification of NH₄Cl-NH₃-H₂O (23%) mixed
5 solutions with different mass fractions.

3200

3600

3360

3400

As can be seen from **Figs.S6-S8** and **Figs.S9-S11**, for KCl-NH₃-H₂O and NH₄Cl-NH₃-H₂O solutions in each group of mixed ammonia systems, with the increasing mass fraction of KCl and NH₄Cl, the highest peaks near 3300 cm⁻¹ are moved to the lower wave number and the peak strengths are all reduced. The peaks near 3400 cm⁻¹ for the 5% and 10% mixed systems are all moved to the high wave number, but when

the ammonia concentration was 23%, the peak near 3400 cm⁻¹ of the KCl-NH₃-H₂O 1 mixture solution was always at 3397 cm⁻¹ and did not move with the increase of the 2 mass fraction of KCl, and the characteristic peak near 3400 cm⁻¹ of the NH₄Cl-NH₃-3 H₂O mixture solution did not move with the increase of the mass fraction of NH₄Cl 4 was always at 3391 cm⁻¹ and a shoulder peak appeared near 3420 cm⁻¹. The addition 5 of KCl and NH₄Cl revealed that the intensities of the spectral components related to 6 ammonia in the region of 3200 cm⁻¹-3300 cm⁻¹ all showed a decreasing trend 7 compared with pure ammonia, which was caused by the expansion of the volume of 8 ammonia solution by the addition of inorganic salts, similar to the dilution of 9 ammonia. This indicates that NH₄Cl and KCl have the same effect on the structure of 10 the ammonia solution. Comparing the Raman spectra of KCl-NH₃-H₂O solution, the 11 NH₄Cl-NH₃-H₂O solution system showed a set of characteristic peaks near the wave 12 number of 1500 cm⁻¹, which is the characteristic peak of the interaction between 13 ammonium ions and water molecules. In the range of 1000 cm⁻¹-2000 cm⁻¹ wave 14 number, the Raman peaks near 1100 cm⁻¹, 1500 cm⁻¹, and 1600 cm⁻¹ wave numbers 15 have an enhanced trend. Therefore, it is analyzed that the changes in Raman spectra in 16 this range are due to the symmetric telescopic vibration of NH₃-H₂O hydrogen 17 bonding and the co-interaction between ammonium ions and water molecules, and the 18 enhancement of the Raman peaks near the wave number of 1500 cm⁻¹ suggests that 19 with the increase of the mass fraction of NH₄Cl in the ammonia solution, the 20 interaction between NH₄⁺ and water molecules is getting stronger and stronger. In 21 addition to this, the peak intensity near 2800 cm⁻¹-3100 cm⁻¹ increases with the 22

increase of NH₄Cl mass fraction, indicating that the N-H vibration of NH₄⁺ is
 continuously enhanced with the increase of NH₄Cl mass fraction.

Since the Raman spectral peak pattern of KCl-NH₃-H₂O solution is similar to 3 that of pure ammonia. In order to observe more clearly the changes in the 4 microstructure of the mixed aqueous solution with the change in solution composition, 5 the peaks were separated using the inverse convolution fitting method. Since the 6 Raman spectrum of the mixed KCl-NH₃-H₂O solution is a superposition of ammonia, 7 water, and the clusters they form, it can be viewed in two parts: the ammonia-related 8 component (denoted by A) and the water-related component. For the ammonia-related 9 component, at least two Gaussian peaks are required for a correct fit, given the 10 obvious asymmetry of the main peak at 3300 cm⁻¹. In the end, four peaks are used to 11 fit all the ammonia-related spectral components, namely, A1, A2, A3, and A4. A1 12 corresponds to the symmetric stretching vibration of the NH₃-H₂O hydrogen bond, A2 13 corresponds to the N-H stretching vibration of the NH₃ dimer, A3 corresponds to the 14 N-H stretching vibration of the monomer NH₃, and A4 corresponds to the 15 antisymmetric vibration of the NH₃-H₂O hydrogen bond. For the water-related 16 components, the symmetric stretching vibrations are assigned to vDAA-OH, vDDAA-17 OH, vDA-OH, vDDA-OH and free OH, respectively, in order to obtain more 18 microstructural information on the intermolecular interactions. Where D is the donor, 19 providing H to form hydrogen bonds with other water molecules, and A is the 20 acceptor, utilizing the lone pair of electrons on oxygen and other water molecules to 21 form bonds. The water molecule contains two hydroxyl groups and two lone pair 22

electrons, i.e., a water molecule that forms four hydrogen bonds is labeled DDAA, a
 free water molecule with one hydrogen atom is labeled DAA, and a free water
 molecule with one pair of lone pair electrons is labeled DDA.

The results of Raman spectral peak splitting of a mixed solution of KCl-NH₃-H₂O with a mass fraction of 5% NH₃ are now analyzed as an example. The results of peak splitting are shown in **Fig.S12**.



7 Fig.S12. Fitting results of solutions with different mass fractions of KCl-NH₃-

8 H₂O(5%): (a) 3.5%-KCl; (b) 7.8%-KCl; (c) 8.7%-KCl; (d) 7.8%-KCl; (e) 12.3%-KCl;

9 (b) 15.5%-KCl; (f) 22%-KCl



1 Fig.S13. Diagram of ammonia-related peak area ratio changes in mixed solutions with

2 different mass fractions of KCl-NH₃-H₂O (5%).



4 Fig.S14. Gaussian peak area ratio of KCl-NH₃-H₂O (5%) mixed solution with

5 different mass fractions.

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As can be seen from **Fig.S13**, the peak areas of A1, A2, A3 and A4 are decreasing as the mass fraction of KCl in the solution increases. As can be seen from **Fig.S14**, the peak areas of DAA-type, DDA-type and free-type hydrogen bonds decreased slightly with the increase of the mass fraction of KCl in the solution, but the change was not significant; the peak areas of DDAA-type hydrogen bonds decreased gradually, and the peak areas of DA-type hydrogen bonds increased gradually. The structure of the hydrogen bonding network in aqueous solution is mainly affected by
the DDAA and DA types of hydrogen bonds, and the decrease of the DDAA type of
hydrogen bonds, which is the representative of the tetrahedral type of hydrogen bonds,
suggests that the degree of damage to the tetrahedral type of hydrogen bonding
network becomes more serious with the increase of the KCl mass fraction. In addition
to this it is also demonstrated that the dissolution of KCl consumes the bulk phase
water in ammonia. For inorganic salts, there is no essential difference between water

Molecular dynamics simulation results: the RDF and coordination number
changes of K-N(A) and N(N)-O(W) in KCl-NH₃-H₂O and NH₄Cl-NH₃-H₂O solutions
are shown in Figs.S15, S16 and Figs.S17 and S18, respectively.



2 Fig.S15. K-N(A) radial distribution function of KCl-NH₃-H₂O solutions with
3 different mass fractions: (a) 5%; (b) 10%; (c) 23%.



Fig.S16. N(N)-O(W) radial distribution function of NH₄Cl-NH₃-H₂O solutions with
 different mass fractions: (a) 5%; (b) 10%; (c) 23%.

As can be seen in Figs.S15 and S16, as the mass fraction of KCl in the mixed 3 ammonia water system continues to increase, the position of the main peak basically 4 remains unchanged, the first hydration radius of K-N(A) is always 2.75 Å, the peak 5 intensity generally shows a decreasing trend, and the area of the first peak also 6 gradually decreases. As the mass fraction of NH₄Cl in the mixed ammonia water 7 system continuously increases, the position of the first peak remains constant at 2.69 8 Å, the first hydration radius of N(N)-N(A) is 2.69 Å, and the peak intensity generally 9 shows an increasing trend. 10



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2 Fig.S17. K-N(A) coordination number of KCl-NH₃-H₂O solution at NH₃ mass
3 fractions of 5%, 10%, and 23% respectively.

From **Fig.S17**, in each mixed ammonia water system, the coordination number of K-N(A) gradually increases with the increase of KCl solution concentration. In the ammonia water solution, alkali metal ions exhibit water selectivity in their first coordination shell and ammonia selectivity in their second coordination shell. With the increase of ammonia water concentration, it can be clearly seen from the figure that at 23% ammonia water concentration, the coordination number of K-N(A) is the highest. This is due to the increasing number of ammonia molecules surrounding the K⁺ ion in the 23% ammonia water system.



Fig.S18. O-O radial distribution function of KCl-NH₃-H₂O solution with different
 mass fraction: (a)5%; (b)10%; (c)23%

Observing **Fig.S18**, it can be seen that the O-O radial distribution function in the mixed ammonia solution exhibits a certain regular variation. As the mass fraction of KCl in each group of ammonia solutions increases, the first peak of *g*O-O(*r*) remains consistently positioned at 2.73 Å, with the peak intensity gradually decreasing.

7 Validation of molecular dynamics simulations with X-ray scattering results: To 8 validate the feasibility of the simulations, we calculated the total F(Q) by summing 9 the 21 partial g(r) functions obtained from MD simulations (weighted by their 10 respective scattering factors) and compared it with the experimental F(Q) from X-ray 1 scattering measurements. In our study, the X-ray scattering method employed faces
2 certain limitations. Elements with low atomic numbers, such as hydrogen (H), have a
3 small X-ray scattering cross-section, resulting in significantly weaker signal
4 intensities compared to elements with high atomic numbers. Additionally, the
5 scattering contributions from low-concentration components can easily be
6 overshadowed by the signals from the major components. Although a liquid water
7 system theoretically should contain 21 independent partial radial distribution
8 functions, not all of them will have distinct signals in practice.

9 The specific procedures are as follows:

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10 (1) In molecular dynamics simulations, the standard formula for combining 11 partial radial distribution functions $g_{\alpha\beta}(r)$ into the total radial distribution function g(r)12 is as follows:

$$g(r) = \sum_{\alpha} \sum_{\beta \ge \alpha} \omega_{\alpha\beta} [g_{\alpha\beta}(r) - 1]$$
(2)

(2) The standard procedure for transforming the radial distribution function g(r)
obtained from molecular dynamics simulations into the structure factor F(Q) through
Fourier transformation is as follows [5]:

17
$$F(Q) = 4\pi\rho \int_{0}^{\infty} r^{2}[g(r) - 1] \frac{\sin(Q_{r})}{Q_{r}} dr$$
(3)

here: Q is the scattering vector ($Q = 4\pi \sin\theta/\lambda$); ρ is the number density of the system (atoms/Å³); g(r) is the total radial distribution function (which needs to be obtained first through weighted summation, as previously mentioned).

(3) Based on the transformation relationships described in Equations (2) and (3),

1 we employ the NumPy library in Python programming for post-processing the results

2 of molecular dynamics simulations.

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3 The processed analysis results are shown in the figure:

5 Fig.S19. The structure factor F(Q) obtained by Fourier transform of the simulation

6 results g(r) for the 10.5K-23N(A) mixed solution



8 Fig.S20. The structure factor F(Q) of the 10.5K-23N(A) mixed solution obtained by
9 X-ray scattering at the BL14B beamline

Fig.S19 shows the structure factor F(Q) of the 10.5% KCl - 23% NH₃ mixture obtained by Fourier transforming the specific g(r) from molecular dynamics simulations. Fig.S20 presents the F(Q) results of the 10.5% KCl - 23% NH₃ mixture obtained by X-ray scattering. In the Q = 2 - 3 Å⁻¹ range, both the experimental and simulated F(Q) exhibit a pronounced main peak. According to the literature [3], a

1 peak at 2.75 Å⁻¹ is commonly observed in the structure functions of pure water and aqueous solutions. The peak position shift (0.25 Å⁻¹) and peak width differences 2 observed in the Q = 2 - 3 Å⁻¹ range between experimental and simulation results 3 mainly originate from the following factors: First, the periodic boundary conditions 4 used in MD simulations may lead to an underestimation of the medium-range order in 5 the system. In future studies, we will take this factor into account and consider 6 increasing the simulation box size. This improvement strategy has been supported by 7 relevant theoretical research. The characteristic peak observed in the molecular 8 dynamics simulation at Q = 4.70 Å⁻¹ is in relatively good agreement with the peak 9 position of 4.80Å⁻¹ measured by X-ray scattering experiments. This minor 10 discrepancy falls within the instrumental resolution error. The characteristic peak 11 corresponds to the deformation vibration mode of the hydrogen bond network in the 12 aqueous solution [7]. 13



15 Fig.S21. The structure factor F(Q) obtained by Fourier transform of the simulation
16 results g(r) for the 5N(N)-23N(A) mixed solution



2 Fig.S22. The structure factor F(Q) of the 5N(N)-23N(A) mixed solution obtained by
3 X-ray scattering at the BL14B beamline

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Fig.S21 shows the structure factor F(Q) of the 5% NH₄Cl - 23% NH₃ mixture
obtained by Fourier transforming the specific g(r) from molecular dynamics
simulations. Fig.S22 presents the F(Q) results of the 5% NH₄Cl - 23% NH₃ mixture
obtained by X-ray scattering.

Both molecular dynamics simulations and X-ray scattering experiments observed 9 significant characteristic peaks in the Q = 2 - 3 Å⁻¹ range, but the peak width in the 10 simulation results was relatively narrower. Additionally, there was a peak shift of Q =11 0.15 Å⁻¹ between the hydrogen bond vibration peaks observed a Q = 4.70 Å⁻¹ in the 12 simulation and Q = 4.55 Å⁻¹ in the experiment. These discrepancies mainly originated 13 from the finite size effect of the simulation system and the incomplete inclusion of the 14 dynamic disorder effects present in the experimental system.

Despite the aforementioned quantitative differences, the simulation and experimental results show a good consistency trend in the key feature region Q = 2 - 5Å⁻¹, which indicates that the current force field parameters used are reasonable for describing the basic structure of the system. We plan to implement the following

1	improvements in our future work [8]:
2	(1) Reasonably expand the simulation box size to reduce the finite size effects
3	introduced by the periodic boundary conditions;
4	(2) Attempt to use polarizable force fields to more accurately describe the
5	electronic polarization interactions between ions and solvents;
6	(3) Refine the calculation of the simulated structure factor to achieve more
7	precise comparison with X-ray data.
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